

Formation of Stripe Patterns in Charged Colloids during Unidirectional Crystallization in the Presence of Impurity Particles

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We examine the spatial distributions of fluorescent-labeled polystyrene (PS) particles added to colloidal silica that resulted after unidirectional crystal growth due to diffusion of pyridine. We find that the PS particles are arranged in a stripe pattern with a submillimeter-sized spacing. The patterning mechanism is attributable to the formation of lamella-shaped crystal grains and exclusion of the PS particles to the crystal grain boundaries.

Charged colloidal particles are stabilized in their aqueous dispersions by long-range electrostatic interparticle interactions. When the interactions are sufficiently strong, the colloids form ordered “crystal” states, where the particles are regularly arranged in body-centered or face-centered cubic lattices.¹

We have previously reported the unidirectional crystallization of charged colloidal silica driven by diffusion of a weak base such as pyridine (Py).^{2–5} The mechanism for this crystallization is explainable as follows.^{2,4} The silica particles have weakly acidic silanol groups (Si–OH) on their surfaces. Dissociation of the silanols is enhanced by addition of Py (Si–OH + Py → Si–O[−] + PyH⁺, where PyH⁺ is a pyridinium cation), resulting in an increase in the particle charge number *Z*. The silica colloids crystallize at sufficiently high *Z*, that is, at large Py concentrations. When an aqueous solution of Py is placed in contact with a noncrystal (low *Z*) silica colloid through a semipermeable membrane, Py molecules diffuse into the colloidal silica, resulting in unidirectional crystallization. Large colloidal crystals with three-dimensional sizes of centimeters at the largest were obtainable through this method.^{3,4}

In recent years, various self-assembled structures formed in multicomponent colloids have attracted much attention. These structures include superlattices⁶ and quasicrystals,⁷ which have a periodicity or quasi-periodicity of the orders of the particle sizes. Ordered structures having larger characteristic length scales are seen, e.g., in phase-separated structures of binary hard-sphere colloids.⁸

Here we examine the structures formed in binary colloids of polystyrene (PS) and silica particles during unidirectional crystallization due to Py diffusion. In related work, we have recently reported that a small number of PS particles (particle volume fraction $\phi = 0.0001$) added to charged colloidal silica crystals ($\phi = 0.03$) was excluded to crystal/noncrystal interfaces during the homogeneous crystallization process.⁹ In the present paper, we report that this exclusion of the PS particles during the unidirectional crystallization results in the formation of submillimeter-sized stripe patterns.

Colloidal silica particles, KE-W10, were purchased from Japan Catalyst Co., Ltd. (Osaka, Japan) and purified by dialysis and ion exchange using a method reported earlier.⁴ Fluorescent-

labeled PS particles, G300, were obtained from Thermo Scientific Co., Ltd. (CA, USA) and deionized using ion-exchange resin beads. Their diameters estimated by dynamic light scattering were 110 and 330 nm, respectively. Their *Z* values, as determined by electrophoretic mobility measurements, were 220 and 1680, respectively.⁸

Unidirectional crystallization experiments were performed as follows. Aqueous dispersions of the KE-W10 silica ($\phi = 0.05$) in the presence or absence of G300 PS particles ($\phi = 0.0001$) were used without any addition of extraneous salt. Reflection spectroscopy showed that crystal structures formed for molar concentrations of Py, [Py] ≥ 50 μM. The colloid sample was introduced into a quartz cell (with inner dimensions of 1 × 10 × 45 mm³) equipped with a poly(tetrafluoroethylene) (PTFE) membrane on one end. The cell was then placed in contact with a reservoir of aqueous Py solution (100 mL, [Py] = 10 mM) to allow the unidirectional crystallization.

Gel-immobilized colloidal crystals were prepared in a manner described previously.⁴ The reaction solutions for the gelation were composed of 0.67 M *N*-methylolacrylamide (gel monomer), 10 mM *N,N'*-methylenebisacrylamide (crosslinker), and 0.1 mg mL^{−1} 2,2'-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] (photoinduced radical polymerization initiator). After the colloidal crystals were grown in the reaction solutions, the samples were gelled under illumination by a 6-W UV lamp for 20 min.

A stereomicroscope, SMZ1500 (Nikon, Japan), was used to observe the crystal grain structures. The spatial distributions of the G300 particles were observed using a fluorescent microscope, ECLIPSE 80i (Nikon) and a confocal laser scanning microscope (LSM), type LSM510 META (Carl-Zeiss, Germany).

Figure 1A shows variations of the crystal length *L* over time *t* for the binary colloid (circles) and silica one-component

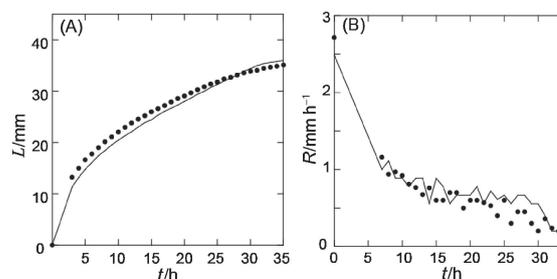


Figure 1. (A) Crystal growth curves and (B) crystal growth rates for the silica + fluorescent PS (filled circles) and the silica one-component (solid line) colloids. Both samples contained the reagents for gelation. Results are averaged values of three independent measurements.

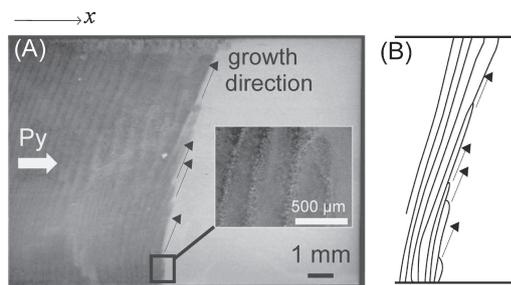


Figure 2. (A) Micrograph showing the crystallization front in the silica + fluorescent PS colloid during unidirectional crystallization. $t = 30$ h. The inset is a fluorescence micrograph of the area indicated by the square. (B) Illustration of the crystal growth mechanism.

colloid (solid line). Both samples contained the gelation reagents. The two curves were not significantly different from each other. That is, the addition of PS particles did not remarkably affect the crystal growth of the silica colloids. Figure 1B presents the growth rates R calculated as slope values of each neighboring data points in the growth curves in Figure 1A.¹⁰

Figure 2A shows a micrograph of the region near the crystallization front of the silica + PS binary colloid ($t = 30$ h); this region covers distances from the PTFE membrane x of 31.9 to 38.5 mm. An arrow in Figure 2A indicates the direction of the Py diffusion. At $x \leq 15$ mm (not shown in the figure), the sample consisted of pillar-shaped crystals that had lengths of a few millimeters in the x direction and submillimeter widths. At larger values of x , the crystals' widths became wider and, as seen in Figure 2A, reached sizes as large as the cell (10 mm) at $x = 30$ mm.¹¹ This wide crystal was composed of thin, lamella-shaped crystal grains. Time-resolved microscopy during the crystallization process revealed that these lamella-shaped crystal grains grew along the crystallization front, as illustrated in Figure 2B. It should be noted that similar crystal growth was occasionally observed for the one-component silica colloid, as well. Thus, it appears that the impurity particles are not requisite for forming the lamella grains. However, colloid samples more or less contain aggregated particles, which should act as impurities on the crystallizations. To elucidate the crystallization mechanism detailed microscopy study for the single colloidal particles is in progress. Movies showing the crystallization processes in the presence and absence of PS are provided as Supporting Information 1 and 2,¹² respectively.

The inset in Figure 2A is a fluorescence micrograph of the area indicated by a square in Figure 2A. It can be clearly seen that the fluorescent PS particles accumulated at the boundaries of the lamella-shaped crystal grains and formed a stripe pattern. In a related result, our recent study showed that PS particles with sizes larger than those of the silica particles were excluded from the colloidal silica crystals upon crystallization.⁹ The present finding strongly suggests that exclusion of the PS particles during the unidirectional crystallization results in the formation of the stripe pattern.

The distributions of the PS particles were examined in more detail by using the LSM on gel-immobilized samples. Figures 3A and 3B show LSM images of the gelled crystal at $x \approx 30$ and 36 mm, respectively. A photograph of the entire

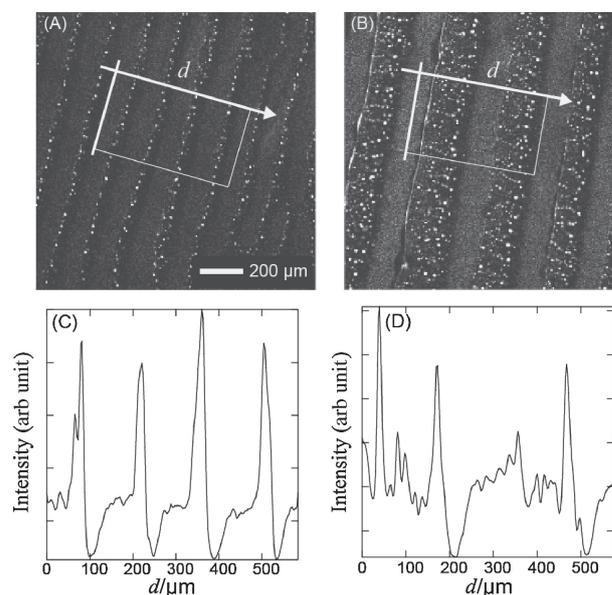


Figure 3. Fluorescence LSM images of the gelled binary colloids (A) at $x = 30$ mm and (B) at $x = 36$ mm. (C, D) Averaged fluorescent intensity profiles for the square regions shown in (A) and (B).

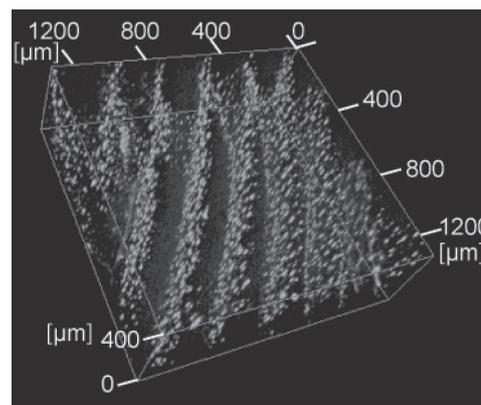


Figure 4. Three-dimensional reconstruction of the stripe pattern in the square region indicated in Figure 3A.

gelled sample is provided in Supporting Information 3.¹² The fluorescent intensity in the square regions shown in Figures 3A and 3B was recorded. The averaged intensity profiles along the direction perpendicular to the stripes (d axes shown in Figures 3A and 3B) are presented in Figures 3C and 3D, respectively. The growth was faster at $x = 30$ mm (Figure 1B; $t \approx 20$ h, $R \approx 0.6$ mm h⁻¹) than at $x = 36$ mm ($t \approx 35$ h, $R \approx 0.2$ mm h⁻¹). Then, the grain width at the former (ca. 150 μm) was smaller than that at the latter (ca. 300 μm).¹¹ The more distinct stripe patterns observed at $x = 30$ mm suggest that the PS particles were more significantly excluded from narrower crystal grains. This finding suggests that the spacing between the stripes can be controlled by changing the crystal growth rate.

Figure 4 shows a three-dimensional reconstruction of the LSM images taken at various focal planes at a 3 μm interval for the region shown in Figure 3A. It is clear that the PS particles

were distributed in a three-dimensional stripe pattern. Hence the focal depth z of the LSM used was variable in the range from $z = 0$ to about $400\ \mu\text{m}$, the image shown in Figure 4 does not cover an entire sample (the thickness: $1000\ \mu\text{m}$). However, a LSM image taken from another side of the sample (i.e., $z = \text{about } 1000\text{--}600\ \mu\text{m}$) also demonstrated a lamellar structure having almost the same periodicity. These observations indicate that the particles are arranged in parallel planes.

The present study shows that interplay of the unidirectional crystal growth and the exclusion of the PS particles from the crystal grains results in the formation of stripe patterns of PS particles. We expect that the present study will be useful for fabricating complex structures in colloidal crystals.

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References and Notes

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- 10 In Figure 1B, the observed R - t plots show deviations from single smooth curves. These deviations are attributable to experimental errors in measuring L values and do not imply that the crystal growths were oscillatory.
- 11 The grain sizes of atomic and molecular crystalline materials are larger when they are formed at slower growth, because further nucleation during the crystal growth is more sufficiently restricted. The observed dependence of the grain size of the colloidal crystals appears to be attributable to the same mechanism.
- 12 Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.